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(54) ELECTROPHOTOGRAPHIC PHOTORECEPTOR

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain an electrophotographic photoreceptor having high sensitivity and high durability by forming a photosensitive layer contg. a specified arylamine compd. on an electrically conductive substrate.

SOLUTION: The electrophotographic photoreceptor has a photosensitive layer contg. an arylamine compd. of the formula on the electrically conductive substrate. In the formula, each of A to F is a benzene ring which may have substituents at least one of which is alkyl, Y is a divalent residue of an arom. hydrocarbon which may have a substituent or a divalent residue of a heterocyclic compd. which may have a substituent, each of R1-R4 is H, cyano, nitro, halogen, alkyl which may have a substituent, aryl which may have a substituent or a heterocyclic group which may have a substituent, R1-R4 may be the same or different, each of n1 and n2 is an integer of 1-4 and each of X1 and X2 is a specified group.

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CLAIMS

[Claim(s)]

[Claim 1]An electro photography photo conductor having a photosensitive layer containing an arylamine system compound expressed with a following general formula [1] on a conductive substrate. [Formula 1]

$$\begin{array}{c} & & \\ & &$$

(A, B, C, D, E, and F among the above-mentioned general formula [1]) Express the benzene ring which may have a substituent, and at least one has an alkyl group among these, and may combine these mutually, may form heterocycle, and;Y, Express the heterocyclic compound residue of the bivalence which may have the aromatic hydrocarbon residue or the substituent of the bivalence which may have a substituent, and;R¹, R², R³, and R⁴, The alkyl group which may have a hydrogen atom, a cyano group, a nitro group, a halogen atom, and a substituent, respectively, Mutually, express the heterocycle group which may have an aryl group which may have a substituent, or a substituent, and these may be the same, or may differ, and;n₁ and n₂, Respectively, the integer of 1 thru/or 4 is expressed, these may be mutually the same or it may differ, and;X ¹ and X ² express the basis shown by the following general formula [2] and a general formula [3], as for these, they may be the same respectively, or may differ. [Formula 2]

[2]

[3]

(R⁵, R⁶, R⁷, R⁸, R⁹, and R¹⁰ among the above-mentioned general formula [2] and [3]) The alkyl group which may have a hydrogen atom, a cyano group, a nitro group, and a substituent, respectively, The heterocycle group which may have an aryl group which may have a substituent, or a substituent is expressed. The pair which consists of the pair and R⁹ which may be mutually the same as for these, or may differ from each other, and consist of R⁶ and R⁷, and R¹⁰, It condenses and the ring group or the heterocycle group may be formed, and when one of such R of a pair of is a hydrogen atom, another side is an aryl group or a heterocycle group.

[Claim 2] The electro photography photo conductor according to claim 1 having a photosensitive layer which contains an arylamine system compound expressed with said general formula [1] as a charge transporting material, and contains non-metal phthalocyanines, metal phthalocyanines, or a screw azo pigment as a charge generating material on a conductive substrate.

[Claim 3] The electro photography photo conductor according to claim 2, wherein a charge generating material is the metal-phthalocyanines compound of at least 1 chosen from a group which consists of following a-c.

a) 9.7 degrees of bragg angles (2theta**0.2 degree) of an X diffraction spectrum, 9.3 degrees of bragg angles (2theta**0.2 degree) of a oxy titanium phthalocyanine b X diffraction spectrum which shows a diffraction peak to 14.2 degrees and 27.3 degrees, 9.2 degrees of bragg angles (2theta**0.3 degree) of a oxy titanium phthalocyanine c X diffraction spectrum which shows a diffraction peak to 13.2 degrees, 26.2

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degrees, and 27.1 degrees, A dihydroxy silicon phthalocyanine compound which has a diffraction peak at 14.1 degrees, 15.3 degrees, 19.7 degrees, and 27.1 degrees [Claim 4]The electro photography photo conductor according to claim 1, wherein n₁ and n₂ are 1.

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DETAILED DESCRIPTION

[Detailed Description of the Invention] [0001]

[Field of the Invention] This invention relates to the photo conductor for electro photography. It is related with the highly efficient photo conductor for electro photography which has a photosensitive layer containing the photoconductivity substance of an organic system in more detail and which is very high sensitivity.

[0002]

[Description of the Prior Art]Conventionally, the photoconductivity substance of inorganic systems, such as selenium, a cadmium sulfide, and a zinc oxide, was widely used for the photosensitive layer of the electro photography photo conductor. However, selenium and a cadmium sulfide need to be collected as poison, since it crystallizes with heat, selenium is inferior to heat resistance, a cadmium sulfide and a zinc oxide are inferior to moisture resistance, and it has a fault, like a zinc oxide does not have print durability, and efforts for development of a new photo conductor are continued. Recently, the research which uses the photoconductivity substance of an organic system for the photosensitive layer of the photo conductor for electro photography progressed, and the some were put in practical use. The photoconductivity substance of an organic system is compared with the thing of an inorganic system, and it has an advantage, like the material with easy manufacture of a photo conductor with easy lightweight membrane formation which can manufacture a transparent photo conductor depending on a kind is pollution—free, and there is.

[0003]These days, since the so-called photo conductor of the functional discrete type which makes a charge carrier's generating and the function of movement share with a separate compound is effective in high-sensitivity—izing, development is in use.

Utilization of the organic system photo conductor by this type is also performed. As charge carrier transportation media, the distributed dissolution of the case where polymers photoconductivity compounds, such as a polyvinyl carbazole, are used, and the low molecule photoconductivity compound may be carried out into binder polymer.

[0004] [Problem(s) to be Solved by the Invention]Since especially the low molecule photoconductivity compound of an organic system can choose the polymer which was excellent in coat nature, flexibility, an adhesive property, etc. as a binder, the photo conductor which was easily excellent in the mechanical property can be obtained (for example, JP,60-196767,A.) JP,60-218652,A, JP,60-233156,A, JP,63-48552,A, JP,1-267552,A, JP,3-39306,B, References, such as JP,3-113459,A, JP,3-123358,A, JP,3-149560,A, JP,6-273950,A, JP,62-36674,A, JP,7-036203,A, publication-number-6-11854, and JP,63-48553,A. However, it was difficult to find out a compound suitable for making a high sensitivity photo conductor. [0005]In the continued request of high-sensitivity-izing, in electrical property Insufficiency [rest potential], When an optical response is bad and carries out repeated use, electrostatic property falls, and it has various problems -- rest potential is accumulated -- As opposed to such a problem, two kinds of specific hydrazone compounds are used together, and the art (JP,61-134767,A) of preventing a rest potential rise without seldom spoiling other characteristics of a photo conductor etc. are reported. However, in respect of the balance of the characteristic, it was not necessarily enough, and the art of raising the characteristic as the whole photo conductor with sufficient balance was searched for. [0006] The semiconductor laser is positively applied in the printer field as a light source, and in this case, since the wavelength of this light source is around 800 nm, development of the photo conductor which has the high sensitivity characteristic also to around 800-nm long wavelength light is desired strongly again. As

a material corresponding to this purpose, JP,59-49544,A, JP,59-214034,A, JP,61-109056,A, JP,61-

171771,A, JP,61-217050,A, JP,61-239248,A, JP,62-67094,A, JP,62-134651,A, JP,62-275272,A, JP,63-198067,A, The material indicated to JP,63-198068,A, JP,63-210942,A, JP,63-218768,A, etc. is mentioned, and the oxy titanium phthalocyanines which have a crystal form respectively suitable as a charge of electro photography photo conductor material are known variously. However, further, from long wavelength light, it is high sensitivity and the photo conductor for electro photography with other good electrical properties was called for.

[0007] This invention is made in order to solve an above-mentioned problem, and there is in providing the 1st high sensitivity and the high durability photo conductor for electro photography of the purpose. The 2nd is the target high sensitivity, and when thickness is thickened, even if rest potential is low enough and carries out repeated use, there is little change of the characteristic and there is in providing the photo conductor for electro photography which was dramatically excellent in endurance. There is the 3rd of the purpose in providing the photo conductor for electro photography in which it is high sensitivity and electrostatic property, a dark decay, rest potential, etc. maintained good balance also in the long wavelength of around 800 nm. It is in providing the quick photo conductor of carrier mobility with the 4th sufficient target response.

[8000]

[Means for Solving the Problem]When this invention persons inquired wholeheartedly about a low molecule photoconductivity compound of an organic system with which it may be satisfied of these purposes, they found out that a specific arylamine system compound was preferred, and resulted in this invention. That is, a gist of this invention is in an electro photography photo conductor having a photosensitive layer containing an arylamine system compound expressed with a following general formula [1] on a conductive substrate.

[0009]

$$\begin{array}{c} & & \\ & &$$

[0010](A, B, C, D, E, and F among the above-mentioned general formula [1]) Express the benzene ring which may have a substituent, and at least one has an alkyl group among these, and may combine these mutually, may form heterocycle, and;Y, Express heterocyclic compound residue of bivalence which may have aromatic hydrocarbon residue or a substituent of bivalence which may have a substituent, and;R¹, R², R³, and R⁴, An alkyl group which may have a hydrogen atom, a cyano group, a nitro group, a halogen atom, and a substituent, respectively, Mutually, express a heterocycle group which may have an aryl group which may have a substituent, or a substituent, and these may be the same, or may differ, and;n₁ and n₂, Respectively, an integer of 1 thru/or 4 is expressed, these may be mutually the same or it may differ, and;X¹ and X² express a basis shown by following general formula [2] and a general formula [3], as for these, they may be the same respectively, or may differ.

[0011]

$$--CR^8 = CR^9CR^{10}$$
 [3]

[0012](R⁵, R⁶, R⁷, R⁸, R⁹, and R¹⁰ among the above-mentioned general formula [2] and [3]) An alkyl group which may have a hydrogen atom, a cyano group, a nitro group, and a substituent, respectively, A heterocycle group which may have an aryl group which may have a substituent, or a substituent is expressed, A pair which consists of a pair and R⁹ which may be mutually the same as for these, or may differ from each other, and consist of R⁶ and R⁷, and R¹⁰, It condenses and a ring group or a heterocycle group may be formed, and when one of such R of a pair of is a hydrogen atom, another side is an aryl group

or a heterocycle group.

[0013]

[Embodiment of the Invention]Hereafter, this invention is explained in detail. The electro photography photo conductor of this invention contains the arylamine system compound expressed with said general formula [1] in a photosensitive layer.

[0014]R¹, R², R³, and R⁴ among said general formula [1], Respectively A hydrogen atom; cyano group; nitro group; fluorine atom, a chlorine atom, Halogen atoms, such as a bromine atom and iodine atom; A methyl group, an ethyl group, propyl, Alkyl groups, such as an isopropyl group; heterocycle groups, such as aryl group; pyridyl groups, such as a phenyl group, a naphthyl group, and a pyrenyl group, and a thienyl group, etc. are expressed, and these may be mutually the same, or it may differ, and a hydrogen atom, a methyl group, and a phenyl group are preferred especially. Among the formula [1], n₁ and n₂ express the integer of 1 thru/or 4, as for these, may be mutually the same, or may differ, respectively.

[0015]These alkyl groups, the aryl group, and the heterocycle group may have a substituent, and as a substituent, Hydroxyl group; Halogen atom; methyl groups, such as a fluorine atom, a chlorine atom, a bromine atom, and iodine atom, Alkyl groups, such as an ethyl group, a propyl group, a butyl group, a hexyl group, and an isopropyl group; A methoxy group, Alkoxy groups, such as an ethoxy basis and a propyloxy group; An allyl group, a vinyl group, Alkenyl groups, such as a butenyl group; Aralkyl group; phenoxy groups, such as benzyl, a naphthyl methyl group, and a phenethyl group, Aryloxy groups, such as a TORIROKISHI group; Aryl alkoxy group; phenyl groups, such as a benzyloxy group and a phenethyloxy group, Aryl groups, such as a naphthyl group; Aryl vinyl group; acetyl groups, such as a styryl group and a naphthyl vinyl group, Acyl groups, such as benzoyl; Dialkylamino groups, such as a dimethylamino group and a diethylamino group, JI substituted amino groups, such as JI heterocyclic amino groups, such as diaralkylamino groups, such as diaryl amino groups, such as a diphenylamino group and a dinaphthylamino group, a dibenzylamino group, and a diphenethyl amino group, a dipyridyl amino group, and a JICHIE nil amino group, and a diarylamino group, - or, Substituted amino groups etc. which changed one side of the substituent of these JI substituted amino groups into an another substituent or hydrogen atom, such as a JI substituted amino group or a mono- substituted amino group, are raised. Various kinds of above-mentioned substituents which an alkyl group, an aryl group, and a heterocycle group have, The singular number or plurality may be sufficient and in two or more cases. These substituents condense mutually and The same R¹, R², In R³ or R⁴, or different R¹, between R² -- or the ring through a single bond, a methylene group, ethylene, a carbonyl group, a vinylidene group, an ECHIRENIREN group, etc. may be formed between different \mathbb{R}^3 and \mathbb{R}^4 , and as long as it is a request, the heterocycle containing an oxygen atom, a sulfur atom, a nitrogen atom, etc. may be formed.

[0016]A, B, C, D, E, and F among said general formula [1], Respectively express the benzene ring, combine these mutually, and A, B, between any 2 persons of C — or the heterocycle containing the nitrogen atom which passed a single bond, a methylene group, ethylene, a carbonyl group, a vinylidene group, an ECHIRENIREN group, etc. among any 2 persons of D, E, and F being formed, and, if it is a request, The heterocycle which furthermore contains an oxygen atom, a sulfur atom, a nitrogen atom, etc. may be formed.

[0017]At least one of these benzene rings has alkyl groups, such as a methyl group, an ethyl group, a propyl group, a butyl group, a hexyl group, and an isopropyl group, as a substituent. The singular number or plurality may be sufficient as the substituent which each benzene ring has, and in two or more cases. It may be mutually the same or may differ, and further, these substituents may be condensed mutually and may form the ring through a single bond, a methylene group, ethylene, a carbonyl group, a vinylidene group, an ECHIRENIREN group, etc. between different positions on each benzene ring.

[0018]Y expresses the heterocyclic compound residue of bivalence, such as aromatic hydrocarbon residue; thienylene of bivalence, such as phenylene, naphthylene, and biphenylene, among said general formula [1], and preferably, It is phenylene or biphenylene and the heterocyclic compound residue with aromatic property of especially heterocyclic compound residue, for example, thienylene, is preferred.

[0019] The residue of these bivalence may have a substituent on a ring or heterocycle, and a substituent, between the positions which the singular number or plurality may be sufficient as, and may be mutually the same in two or more cases, or may differ, and condense these substituents mutually further and from which it differs on each ring — or a ring or heterocycle may be formed between another rings. Furthermore, those rings by which condensation formation was carried out may also have a substituent. As a substituent which the residue or the ring by which condensation formation was carried out of the above—mentioned bivalence

has, Alkyl groups, such as a methyl group, an ethyl group, a propyl group, a butyl group, a hexyl group, and an isopropyl group; A phenyl group, aryl group [, such as a naphthyl group,]; — cyano group; — alkoxycarbonyl group; — aryloxy carbonyl group; — nitro group; — halogen atoms, such as a fluorine atom, a chlorine atom, a bromine atom, and iodine atom, etc. are raised.

[0020]X ¹ expresses the basis shown with a following general formula [2] among a general formula [1], X ² expresses the basis shown with a following general formula [3], and these may be the same respectively or may differ.

[0021]

[Formula 5]

-CR5-CR6CR7

[2]

[3]

[0022]R⁵, R⁶, R⁷, R⁸, R⁹, and R¹⁰ among a general formula [2] and [3], Respectively A hydrogen atom; cyano group; nitro group; methyl group, an ethyl group, propyl, Alkyl groups, such as an isopropyl group; heterocycle groups, such as aryl group; pyridyl groups, such as a phenyl group, a naphthyl group, and a pyrenyl group, and a thienyl group, etc. are expressed, and these may be mutually the same, or it may differ, and a hydrogen atom, a methyl group, and a phenyl group are preferred especially. [0023]These alkyl groups, an aryl group, and a heterocycle group may have a substituent, and as a substituent, Hydroxyl group; Halogen atom; methyl groups, such as a fluorine atom, a chlorine atom, a bromine atom, and iodine atom, Alkyl groups, such as an ethyl group, a propyl group, a butyl group, a hexyl group, and an isopropyl group; A methoxy group, Alkoxy groups, such as an ethoxy basis and a propyloxy group; An aliyl group, a vinyl group, Alkenyl groups, such as a butenyl group; Aralkyl group; phenoxy groups, such as benzyl, a naphthyl methyl group, and a phenethyl group, Aryloxy groups, such as a TORIROKISHI group; Aryl alkoxy group; phenyl groups, such as a benzyloxy group and a phenethyloxy group, Aryl groups, such as a naphthyl group; Aryl vinyl group; acetyl groups, such as a styryl group and a naphthyl vinyl group, Acyl groups, such as benzoyl; Dialkylamino groups, such as a dimethylamino group and a diethylamino group, JI substituted amino groups, such as JI heterocyclic amino groups, such as diaralkylamino groups, such as diaryl amino groups, such as a diphenylamino group and a dinaphthylamino group, a dibenzylamino group, and a diphenethyl amino group, a dipyridyl amino group, and a JICHIE nil amino group, and a diarylamino group, -− or, Substituted amino groups etc. which changed one side of a substituent of these JI substituted amino groups into an another substituent or a hydrogen atom, such as a JI substituted amino group or a monosubstituted amino group, are mentioned.

[0024] Various kinds of above-mentioned substituents which an alkyl group, an aryl group, and a heterocycle group have, The singular number or plurality may be sufficient and in two or more cases. These substituents condense mutually and R⁵, R⁶, In R⁷, R⁸, R⁹, or R¹⁰, between R⁵, and R⁶ and R⁷ or between R⁸, and R⁹ and R¹⁰, A ring through a single bond, a methylene group, ethylene, a carbonyl group, a vinylidene group, an ECHIRENIREN group, etc. may be formed, and as long as it is a request, heterocycle containing an oxygen atom, a sulfur atom, a nitrogen atom, etc. may be formed. However, when one of a pair of R which consists of a pair and R⁹ which consist of R⁶ and R⁷, and R¹⁰ is a hydrogen atom, another side is an aryl group or a heterocycle group. A pair which consists of a pair and R⁹ which consist of R⁶ and R⁷, and R¹⁰, Condense, may form a ring group or a heterocycle group, and a formed ring group or a heterocycle group further, Alkyl groups, such as a methyl group, an ethyl group, a propyl group, a butyl group, a hexyl group, and an isopropyl group; A phenyl group, Aryl groups, such as a naphthyl group; it may have substituents, such as halogen atoms, such as an alkoxycarbonyl group, an aryloxy carbonyl group, a cyano group, a nitro group; fluorine atom, a chlorine atom, a bromine atom, and iodine atoms.

[0025]It enumerates about an arylamine system compound expressed with a general formula [1] below for illustration of the example of representation. Of course, an arylamine system compound used for this invention is not limited only to an example of these representation. In the following illustration, a general formula [1] was imitated, and it divided and displayed on a structural formula of a compound, and the substituent X1 and X2, and when it was a compound from which only a substituent is different, only the substituent X1 and X2 were displayed about a compound of the 2nd henceforth.

[0026] [Formula 6]

[0027] [Formula 7]

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[0029] [Formula 9]

[0030] [Formula 10]

[0032] [Formula 12]

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[0035] [Formula 15]

[0036] [Formula 16]

[0037] [Formula 17]

[0038] [Formula 18]

[0039] [Formula 19]

[0040] [Formula 20]

[0041] The arylamine system compound expressed with said general formula [1] can be manufactured using a publicly known method. For example, it is the method of obtaining the target compound, by performing a publicly known carbonyl introduction reaction and a Wittig reaction, using a publicly known arylamine system compound as a raw material. When this method is explained in detail, these reactions are first shown by the following reaction formula.

[0042]

[Formula 21]

[0043]In the reaction formula showing an above-mentioned carbonyl introduction reaction and Wittig reaction, The ring A, B, and C, D, E and F, basis R¹, R², R³, R⁴, R⁵, R⁶, R⁷, R⁸, R⁹, R¹⁰, Y, X ¹, X ², subscript n_1 , and n_2 have the same meaning as the thing in the above-mentioned general formula [1], [2], and [3].

[0044]In the case of R⁵=R⁸=H: 1) The arylamine system compound expressed with a general formula [4] or [6], If it is made to react to formylation agents, such as N.N-dimethylformamide and N-methylformanilide, under existence of phosphorus oxychloride, the aldehyde object shown by a general formula [5] or [7] will be acquired. An inertness solvent can also be used for reactions, such as O-dichlorobenzene and benzene, although a formylation agent can be used for an overlarge and it can also serve as a reactional solvent in that case.

[0045]2) An arylamine system compound which is expressed with a general formula [4] or [6] in R⁵ and R⁸! =H, The bottom of Lewis acid existence, such as an aluminium chloride, ferric chloride, and zinc chloride, nitrobenzene, A ketone body expressed with a general formula [5] or [7] is obtained among solvents, such as dichloromethane and a carbon tetrachloride, by making it react to an acid chloride expressed with an acid chloride and general formula Cl–CO–R⁸ which are expressed with general formula Cl–CO–R⁵. [0046]Subsequently, an aldehyde object or a ketone body which was obtained by a carbonyl introduction reaction and which is expressed with a general formula [5] or [7], In a publicly known organic solvent [inertness / reactions /, such as N.N–dimethylformamide, N,N–dimethylacetamide, a tetrahydrofuran, dioxane benzene, and toluene,], General formula R⁶R⁷ CHQ or R⁹R¹⁰ CHQ (among both types) Q shows halogen atoms, such as a chlorine atom and a bromine atom, — a halogenated compound expressed — triphenyl phosphine or doria — RUKOKI silyne compound (R¹⁵O) ₃P (R¹⁵ — a methyl group.) Alkyl groups, such as an ethyl group, are expressed. About a Wittig reagent produced by making act, 10–200 ** is 20–100 ** in temperature preferably, An arylamine system compound expressed with a general formula [1] or [6] is obtained by making it react under existence of publicly known basic catalysts, such as butyl lithium,

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phenyllithium, sodium methoxide, a sodium ethoxide, and potassium t-butoxide.

[0047]At this time, either of the mixtures of the Sis object, a transformer object and the Sis object, and a transformer object is obtained as an arylamine system compound expressed with a general formula [1]. In these reactions, it is also possible to acquire a high grade object after each end of a process or an end of a whole process by publicly known refining means, such as recrystallization refining, reprecipitation refining, sublimation refining, and column purification, depending on the case.

[0048]An electro photography photo conductor of this invention has one sort or a photosensitive layer (photoconductive layer) contained two or more sorts for an arylamine system compound expressed with the above-mentioned general formula [1] on a conductive substrate. Carrying out a deer, an arylamine system compound expressed with a general formula [1] shows performance which was extremely excellent as an organic photoconductor. When it uses as a charge transport medium especially, a photo conductor which was excellent in endurance by high sensitivity is given.

[0049]In an electro photography photo conductor of this invention, if a photosensitive layer contains an arylamine system compound expressed with the above-mentioned general formula [1], it can take arbitrary gestalten. Namely, a charge transport layer which contains a charge transporting material which conveys a charge generating layer and a charge carrier containing a charge generating material which generates a charge carrier at very high efficiency if a photosensitive layer absorbs light, this order — or what is called distributed type in which a layer which distributed particles of a charge generating material was formed to the carrier fluid inside of the body as which what is called a lamination type that carried out laminating formation to reverse order may be sufficient and which carries out and contains a charge transporting material may be sufficient.

[0050]In this invention, an arylamine system compound expressed with the above-mentioned general formula [1], When using into [charge transport layer] a lamination type photosensitive layer which consists of two-layer [of a charge generating layer and a charge transport layer], especially sensitivity is high, rest potential is small, and when repeated use is carried out, there can be little change of surface potential, fall of sensitivity, accumulation of rest potential, etc., and a photo conductor excellent in endurance can be obtained.

[0051]As a charge generating material used for an electro photography photo conductor of this invention, there is no restriction in particular — selenium, a selenium tellurium alloy, and *****-** — base — an alloy. Inorganic photoconductivity particles, such as a cadmium sulfide and an amorphous silicon; Non-metal phthalocyanines, Organic photoconductivity particles, such as metal content phthalocyanine, peri non system paints, a thioindigo, Quinacridone, perylene system paints, anthraquinone system paints, monoazo paints, screw azo pigment, tris azo pigment, polyazo system paints, and cyanine system paints, are mentioned. Various organic coloring matter, such as polycyclic quinone, pyrylium salt, thio pyrylium salt, indigo, anthanthrone, and the Piran TRON, can also be used.

[0052]In these charge generating materials, non-metal-phthalocyanines; copper, indium chloride, Metal content phthalocyanine which metal, such as a gallium chloride, tin, oxy titanium, zinc, and vanadium, or an oxide of those, and a chloride configurated; azo pigments, such as monoazo, screwazo, trisazo, and a polyazo system, are preferred.

[0053]Especially, since a photo conductor whose sensitivity to a laser beam improved is obtained when it combines with an arylamine system compound shown by said general formula [1], metal content phthalocyanine and non-metal phthalocyanines are preferred. Especially 9.7 degrees of bragg angles (2theta**0.2 degree) of a X diffraction spectrum, Oxy titanium phthalocyanine which shows a diffraction peak to 14.2 degrees and 27.3 degrees, b) 9.3 degrees of bragg angles (2theta**0.2 degree) of an X diffraction spectrum, Oxy titanium phthalocyanine which shows a diffraction peak to 13.2 degrees, 26.2 degrees, and 27.1 degrees, or 9.2 degrees of bragg angles (2theta**0.3 degree) of c X diffraction spectrum, An electro photography photo conductor containing a dihydroxy silicon phthalocyanine compound which has a diffraction peak at 14.1 degrees, 15.3 degrees, 19.7 degrees, and 27.1 degrees, Rest potential is low, and electrostatic property is high, and change by repetition is small at high sensitivity, and since electrifying stability which influences image concentration especially is good, it can use as a high durability photo conductor. It is especially suitable for a photo conductor for semiconductor laser beam printers from sensitivity of a 750-850-nm field being high.

[0054] Although a manufacturing method in particular of oxy titanium phthalocyanine of said a is not limited, it is manufactured, for example by the following methods.

1 It is indicated in the example 1 of JP,62-67094,A manufacture. [II]A manufacturing method of a mold crystal. That is, heat alt.phtalo dinitrile and a halogenide of titanium, they are made to react in an inactive

organic solvent, and, subsequently it hydrolyzes.

2 About oxy titanium phthalocyanine of various crystal forms, it is inside of direct or organic acid solvent, sulfuric acid, or formula R-SO₃H (R among a formula). Aliphatic series or aromatic residue which may have a substituent is expressed. It heat-treats by a sulfonation thing expressed, or heat-treats with a mixed solvent of an insoluble organic solvent and water after that depending on the case.

3 By request, emit to concentrated sulfuric acid into after-dissolution ice water beforehand, or heat-treat by the above-mentioned sulfonation thing after amorphous-izing by publicly known methods, such as the mechanical grinding methods, such as a paint shaker, a ball mill, and a SANDOGU lined mill, or heat-treat with a water-immiscible organic solvent and a mixed solvent of water.

4 In processing with an above-mentioned sulfonation thing, use together the mechanical grinding methods, such as a paint shaker, a ball mill, and a SANDOGU lined mill, instead of heat-treatment.

[0055] In this invention, two or more sorts of phthalocyanine compounds can also be used together as a

charge generating material. For example, 9.7 degrees of bragg angles (2theta**0.2 degree) of the aforementioned X diffraction spectrum, 9.3 degrees of bragg angles (2theta**0.2 degree) of oxy titanium phthalocyanine which shows a diffraction peak to 14.2 degrees and 27.3 degrees, and an X diffraction spectrum, Oxy titanium phthalocyanine which shows a diffraction peak to 13.2 degrees, 26.2 degrees, and 27.1 degrees is used together, Or 9.7 degrees of bragg angles (2theta**0.2 degree) of the aforementioned X diffraction spectrum, 8.5 degrees of bragg angles (2theta**0.2 degree) of oxy titanium phthalocyanine which shows a diffraction peak to 14.2 degrees and 27.3 degrees, and an X diffraction spectrum, It is preferred to use together dichlorotin phthalocyanine which shows a diffraction peak to 12.2 degrees, 13.8 degrees, 16.9 degrees, 22.4 degrees, 28.4 degrees, and 30.1 degrees in respect of sensitivity.

[0056]An electro photography photo conductor of this invention can be manufactured in accordance with a conventional method. Namely, an above-mentioned charge generating material and/or a charge transporting material are dissolved into a suitable solvent with a binder, It can manufacture by applying coating liquid produced by adding well-known additive agents, such as a suitable sensitization color, an electronic suction nature compound, and a plasticizer, on a conductive substrate, drying if needed, and making a photosensitive layer of predetermined thickness form. What is necessary is just to apply coating liquid containing both materials, when it is a distributed photosensitive layer although it is necessary to prepare as respectively separate coating liquid in the case of a lamination type photosensitive layer which consists of two-layer [of a charge generating layer and a charge transport layer] and it needs to apply a charge generating material and a charge transporting material one by one. But it is also possible for a charge generating layer of a lamination type photosensitive layer not to be based on spreading, but to form by vacuum evaporation.

[0057]As binder resin used for a charge generating layer in a lamination type photosensitive layer, For example, polyester resin, polyvinyl acetate, polyester polycarbonate, A polyvinyl aceto acetal, polyvinyl propional, a polyvinyl butyral, phenoxy resin, an epoxy resin, urethane resin, cellulose ester, cellulose ether, etc. are mentioned. If particles, such as a charge generating material, can be made into a dispersion layer of a form bound with various binder resin, there will be no restriction. Besides these, binder resin, such as a polymer of vinyl compounds, such as styrene, vinyl acetate, VCM/PVC, acrylic ester, methacrylic acid ester, vinyl alcohol, and ethyl vinyl ether, and a copolymer, polyamide, and a silicone resin, can also be used. A use rate of a charge generating material in this case receives binder resin 100 weight section, 20 to 2000 weight section, is depended and is usually preferably chosen from the range of 33 to 500 weight section.

[0058]As binder resin used for a charge transport layer in the case of a lamination type photosensitive layer, or binder resin used as a matrix in the case of a distributed photosensitive layer, Compatibility with a charge transporting material is good, and a charge transporting material crystallizes after coat formation, or, Polymer which does not carry out phase separation is preferred, and For example, styrene, vinyl acetate, A polymer and copolymers of a vinyl compound, such as VCM/PVC, acrylic ester, methacrylic acid ester, and butadiene, A polyvinyl acetal, polycarbonate, polyester, polyester carbonate, Various polymer, such as polysulfone, polyimide, polyphenylene oxide, polyurethane, cellulose ester, cellulose ether, phenoxy resin, a silicone resin, and an epoxy resin, is mentioned, and these partial bridge construction hardened materials can also be used. the amount of binder used receives a charge transporting material — 0.5 – 30 weight twice — it is a twice [0.7 – 10 weight] as many range as this preferably.

[0059] As a solvent for coating liquid preparation, a tetrahydrofuran, 1,4-dioxane, Ketone, such as ether, such as dimethoxyethane, methyl ethyl ketone, the 4-methoxy-4-methylpentanone 2, and cyclohexanone;

Toluene, Aromatic hydrocarbon, such as xylene; N.N-dimethylformamide, acetonitrile, Ester species, such as aprotic polar solvent; ethyl acetate, such as N-methyl pyrrolidone and dimethyl sulfoxide, methyl formate, and methyl-cellosolve acetate; chlorinated hydrocarbon, such as a dichloroethane and chloroform, is mentioned. Of course, it is necessary to choose from these what dissolves a binder. In the case of a photosensitive layer containing charge transporting materials, such as an arylamine system compound, it is also required to choose a solvent in which these are dissolved.

[0060]Next, as color coloring matter added by case in this invention, For example, a quinone color and cyanine dye, such as thiazine dye, such as triphenylmethane colors, such as Methyl Violet, brilliant green, and Crystal Violet, and methylene blue, and quinizarine, a kinky thread RIUMU salt, a thia kinky thread RIUMU salt, a benzo kinky thread RIUMU salt, etc. are mentioned.

[0061]As an arylamine system compound and an electronic suction nature compound which forms an electron donor acceptor complex, For example, chloranil, a 2, 3-dichloro-1, 4-naphthoquinone, 1-nitroanthraquinone, 1-chloro-5-nitroanthraquinone, 2-chloroanthraquinone, quinone [, such as phenanthrene quinone,]; -- aldehyde [, such as 4-nitrobenzaldehyde,]; -- 9-benzoylanthracene. Indanediones, 3,5-dinitrobenzophenone, 2,4,7-trinitro fluorenone, Ketone, such as 2,4,5,7-tetranitro fluorenone, 3,3', and 5,5'-tetra nitrobenzo phenon; Phthalic anhydride, Acid anhydrides, such as 4-chloronaphthalic anhydride; Tetracyanoethylene, Tele FUTARARU malononitrile, 9-anthrylmethylidenemalononitrile, Cyano compound;3-benzal phthalides, such as 4-nitro benzal malononitrile and 4-(p-nitrobenzoyloxy) benzal malononitrile, Electronic suction nature compounds, such as phthalides, such as 3-(alpha-cyano p-nitro benzal) phthalide and 3-(alpha-cyano p-nitro benzal)-4,5,6,7-tetrachlorophthalide, are mentioned.

[0062]A photosensitive layer of a photo conductor for electro photography of this invention may contain a well-known plasticizer in order to raise membrane formation nature, flexibility, and a mechanical strength. Specifically, phthalic ester, phosphoric ester, an epoxy compound, a chlorinated paraffin, chlorination fatty acid ester, aromatic compounds like methylnaphthalene, etc. are mentioned.

[0063]A charge generating layer in the case of a lamination type photosensitive layer besides the above-mentioned various additive agents may contain various additive agents, such as a leveling agent for improving spreading nature, an antioxidant, and a sensitizer, if needed. A charge generating layer may be a vacuum evaporation film of the above-mentioned charge generating material again. 0.15-0.8 micrometer 0.1-2-micrometer is 0.05-5 micrometers usually more preferably preferred for thickness of a charge generating layer preferably.

[0064]A charge transport layer in the case of a lamination type photosensitive layer may contain various additive agents, such as an antioxidant and a sensitizer, and other publicly known charge transporting materials, for example, other arylamine compounds which have the performance outstanding as an organic photoconductor, a hydrazone compound, and a stilbene compound if needed. In addition to this, a mechanical strength of a coat and various additive agents for durability enhancement can be used for a charge transport layer. As such an additive agent, various stabilizer, a fluid grant agent, a cross linking agent, etc. besides the above-mentioned plasticizer are mentioned. 27-40 micrometers 10-45-micrometer are 10-60 micrometers usually more preferably preferred for thickness of a charge transport layer preferably.

[0065] The above-mentioned plasticizer for improving membrane formation nature, flexibility, a mechanical strength, etc. also in the case of a distributed photosensitive layer, etc. A leveling agent for improving a distributed adjuvant for an additive agent for controlling rest potential and improvement in dispersion stability and spreading nature, a surface-active agent, for example, silicone oil, fluorine system oil, and other additive agents may be added. 10–45 micrometers 5–50-micrometer are usually preferably preferred for thickness of a distributed photosensitive layer.

[0066]In the case of a distributed photosensitive layer, particle diameter of a charge generating material needs a small enough thing, and is more preferably used at 0.5 micrometer or less 1 micrometer or less. Although it is 0.5 to 50% of the weight of a range, for example, if too small, sufficient sensitivity will not be obtained, but if there is too much quantity of a charge generating material distributed in a photosensitive layer, it will have evils, such as a fall of electrostatic property, and a fall of sensitivity, and will be more preferably used in 1 to 20% of the weight of the range.

[0067]In this invention, coating methods for forming a predetermined photosensitive layer include a spray coating method, the spiral applying method, the ring applying method, a dip coating method, etc. As a spray coating method, although there are an air spray, airless spray, an electrostatic air spray, electrostatic airless spray, a rotation atomization type electrostatic spray, hot spraying, hot airless spray, etc., In

[considering the degree of microatomization for obtaining uniform thickness, deposit efficiency, etc.,] a rotation atomization type electrostatic spray, An electro photography photo conductor which was excellent in the homogeneity of thickness with synthetically high deposit efficiency can be obtained by conveying continuously, without opening an interval in the shaft orientations, rotating a transportation method currently indicated by republication common No. 805198 [one to] gazette, i.e., a cylindrical work. [0068]A method using a pouring—in spreading machine or a curtain spreading machine currently indicated by JP,52–119651,A as a spiral applying method, There are a method of continuing in the shape of a muscle and making a paint flying from a minute opening part currently indicated by JP,1–231966,A, a method using a multi–nozzle body currently indicated by JP,3–193161,A, etc.

[0069]In a dip coating method, coating liquid beforehand adjusted to immersion is used. namely, total-solids concentration, such as a photo conductor and binder resin, — not less than 25% — more — desirable — 40% or less and viscosity — usually — 50 – 300 sentimental POAZU — coating liquid is adjusted so that it may become 100 – 200 sentimental POAZU preferably. Here, although viscosity of coating liquid is substantially decided by kind of binder resin, and its molecular weight, since resin's own mechanical strength will fall if a molecular weight is not much low, it is preferred [viscosity] to use binder resin with a molecular weight of a grade which does not spoil this.

[0070]It is good to adjust drying temperature time so that a coat may be dried after that and required and sufficient desiccation may be performed. A range of 110–170 ** of drying temperature is 100–250 ** usually 120–140 ** still more preferably preferably. As a drying method, hot air drying equipment, a steam drying machine, a ultrared ray dryer, a far infrared dryer, etc. can be used.

[0071] Thus, a photo conductor formed for improvement of an electrical property and a mechanical characteristic, It cannot be overemphasized that it may have interlayers, such as a barrier layer, a glue line, and a blocking layer, and may have surface layers, such as a protective layer, on the surface of a photosensitive layer between photosensitive layers or between a photosensitive layer and a base material if needed.

[0072]As an interlayer, for example An aluminum anode oxide layer, an aluminum oxide, Organic layers, such as inorganic layers, such as aluminium hydroxide, polyvinyl alcohol, casein, a polyvinyl pyrrolidone, polyacrylic acid, cellulose, gelatin, starch, polyurethane, polyimide, and polyamide, are used. As a surface layer, protective layers, such as ultraviolet curing resin, are used, for example.

[0073]As a conductive substrate in which a photosensitive layer is formed, each thing adopted as an electro photography photo conductor can use it. A drum which specifically consists of metallic materials, such as aluminum, stainless steel, copper, and nickel, a sheet, or a laminated object of these metallic foils; by vacuum evaporation etc. Polyester film which provided conductive layers, such as aluminum, copper, palladium, tin oxide, and indium oxide, in the surface, Insulating support bodies, such as paper; A plastic film which applied conductive substances, such as metal powder, carbon black, copper iodide, and a polymer electrolyte, with a suitable binder, and carried out electric conduction processing, A sheet and a drum of a plastic which contained conductive substances, such as; metal powder, such as a plastic drum, paper, and a paper tube, carbon black, and carbon fiber, and became conductivity; a plastic film and a belt which carried out electric conduction processing with conductive metallic oxide, such as tin oxide and indium oxide, are mentioned. Especially, it is a base material with preferred metal drums, such as aluminum.

[0074] Hereafter, an example explains this invention still in detail.

(Example of manufacture)

An arylamine compound shown with a <u>carbonyl introduction reaction</u> following formula [0075] [Formula 22]

[0076]6.4 g was dissolved in DMF100mL. Temperature up was carried out to 60 **, and 4.6 g of phosphorus oxychloride was dropped (65 ** **5 **). It was made to react at 65 ** **5 ** for 2 hours, and in TLC, after the ending reaction check, it cooled radiationally and the reaction solution was emitted into the potassium hydroxide solution (KOH10g / water 500g). The ** exception carried out the depositing solid

after neglect one whole day and night, and it ****(ed) twice with the water of 0.5L (it checks that filtrate is neutral). It was made to dry at 60 ** under decompression for 30 hours, and was made to dissolve in DMF100ml. The formyl object and the dusky yellow solid 6g which emit to the water 0.5L, and a ** exception carries out the depositing solid, dry at 60 ** under decompression for 30 hours, and are shown with a following formula were obtained.

[0077]

[Formula 23]

[0078] The Wittig reagent shown with the <u>Wittig reaction</u> above-mentioned formyl object 3.5g and a following formula [0079]

[Formula 24]

[0080]3.7 g was dissolved in THF50mL and t-BuOK 1.6g was added little by little (20 ** **5 **). It agitated for 1 hour, and the reactant was emitted to methanol 200mL and the ** exception carried out the depositing solid. The solid was dried at 60 ** under decompression, the column refined, it was shown by the structural formula first held as the above-mentioned example of representation, and the 1st substituent X1 and the compound 2.0g which has X2 were obtained. The infrared absorption spectrum was shown in drawing 1.

[0081](Example 1)

In a formation X diffraction spectrum of a charge generating layer, 9.3 degrees of bragg angles (2theta**0.2 degree), 10.6 degrees, 13.2 degrees, 15.1 degrees, 15.7 degrees, 16.1 degrees, 20.8 degrees, 1.0 copy of titanium oxy phthalocyanine pigment in which 23.3 degrees, 26.2 degrees, and a diffraction peak strong against 27.1 degrees are shown, After carrying out distributed processing with a Sand grinder in addition to 14 copies of dimethoxyethane, 14 copies of dimethoxyethane and 4-methoxy-4-methylpentanone 2 (made by Mitsubishi Chemical) 14 copy are added and diluted, 0.5 copy of polyvinyl butyral (the DENKI KAGAKU KOGYO [K.K.] K.K. make, trade name DENKA butyral #6000-C), They are six copies of dimethoxyethane, and the 4-methoxy-4-methylpentanone 2 about 0.5 copy of phenoxy resin (made in Union Carbide, trade name UCAR(trademark registration) PKHH). It mixed with liquid which dissolved in a mixed solvent of six copies, and dispersion liquid were obtained. After applying these dispersion liquid with a wire bar on an amino deposition layer vapor-deposited by polyester film of 75-micrometer thickness so that weight after desiccation may become 0.4 g/m², it dried and a charge generating layer was made to form. [0082]Polycarbonate resin indicated to be 70 copies of arylamine system compounds (compound which is shown by structural formula first held as the above-mentioned example of representation, and has the 1st substituent X1 and X2) compounded in said example of manufacture on a charge generating layer in which a charge transport layer was formed thus formed with a following formula [0083] [Formula 25]

$$\begin{array}{c|c} & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & &$$

x:y = 1:1

[0084] The photo conductor for electro photography of what is called a lamination type which applies the coating liquid which dissolved 100 copies in 900 copies of mixed solvents which are mainly concerned with a tetrahydrofuran, dries, makes the charge transport layer of 20 micrometers of thickness form, and has a photosensitive layer which consists of two-layer was obtained.

[0085]The following electrical property was measured about <u>evaluation of a photo conductor</u>, thus the obtained photo conductor for electro photography.

Sensitivity, i.e., a reduction-by-half light exposure, : (1) A reduction-by-half light exposure carries out negative electrification of the photo conductor according to the corona current of 50microA first in a dark place, Subsequently, it exposed with the 780-nm light (exposure energy 10 microwatt/cm²) obtained by the interference filter through 20 luxs white light, and asked by measuring the light exposure taken for surface potential to decline from -550V to -275V. Measured value was 0.43microJ/cm².

(2) Rest potential: it was −9V when surface potential when exposure time was made into 9.9 seconds was further measured as rest potential. Although this operation was repeated 2000 times, the rise of rest potential was not seen.

[0086](Example 2) It was shown instead of an arylamine system compound used in Example 1 by structural formula held to the 2nd as the above-mentioned example of representation, and an electro photography photo conductor was obtained like Example 1 except using the 1st substituent X1 and a compound which has X2. Thus, sensitivity and rest potential were measured about an obtained photo conductor for electro photography. A measurement result is shown in the 1st after-mentioned table.

[0087](Comparative example 1) The comparison compound 1 shown with a following formula instead of an arylamine system compound used in Example 1 [0088] [Formula 26]

比較化合物 1

[0089]The electro photography photo conductor was obtained like Example 1 except *******. The result of having measured sensitivity and rest potential is shown in the 1st after-mentioned table. [0090](Comparative example 2) The comparison compound 2 shown with a following formula instead of the arylamine system compound used in Example 1 [0091] [Formula 27]

比較化合物 2

[0092]Although it was going to obtain an electro photography photo conductor like Example 1 except *******, after dissolving in polymer liquid, when it applied, a solid deposited on a spreading side during solvent desiccation, and measurement of an electrical property was not completed.
[0093](Comparative example 3) The comparison compound 3 shown with a following formula instead of an arylamine system compound used in Example 1 [0094]

[Formula 28] 比較化合物 3

[0095]Although it was going to obtain the electro photography photo conductor like Example 1 except ********, and you tried to make it dissolve in polymer liquid, it did not dissolve thoroughly and measurement of the electrical property was not completed.
[0096]

1st Table Example 1 Example 1 Comparative—Example 1 Sensitivity (MuJ/cm²) 0.43 0.41 0.43 Rest Potential (V) 9 9 34[0097]Therefore, it turns out that especially an arylamine system compound of Examples 1 and 2 is excellent in rest potential compared with a charge transport compound of the comparative example 1, and it excels also in sensitivity. Compared with a compound of the comparative examples 2 and 3, it turns out that it excels in the solubility of a coating solution, and compatibility with PORIKA.

[0098]

[Effect of the Invention] Since the photo conductor for electro photography of this invention has high compatibility with polymer, and the rest potential leading to a fogging is small and there is little especially optical fatigue, accumulation of the rest potential by use and change of surface potential and sensitivity have repeatedly the feature of excelling in endurance small.

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] The infrared-absorption-spectrum figure of the arylamine derivative obtained in the example of manufacture.

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DRAWINGS

[Drawing 1]

